REACTIVITY AND TAUTOMERISM IN THE AZOLIDINE SERIES

II.* SYNTHESIS OF 2-ALKYLRHODANINES

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A method for the synthesis of 2-alkylrhodanines was developed on the basis of the reaction of rhodanine salts with alkyl halides in nonpolar or slightly polar solvents.

It has been established [1, 2] that 2-alkyl- and 3-alkylrhodanines are formed by the reaction of rhodanine and its 5-benzylidene derivatives with alkyl halides in polar solvents in the presence of hydrogen halide acceptors. The ratio of the alkylation products is determined by the nature of the solvent. The 3-alkyl-derivative fraction increases with the solvent polarity.

In the course of a further investigation of the alkylation of rhodanines we studied the reaction of rhodanines with alkyl halides in nonpolar and slightly polar solvents (hexane, dioxane, carbon tetrachloride, benzene, chloroform, and ethyl acetate) using triethylamine, pyridine, alkalis, alkali metals, and sodium hydride as hydrogen halide acceptors. The reaction was followed by means of thin-layer chromatography on aluminum oxide and indicated that only 2-alkyl derivatives are formed in chloroform. The formation of 1-5% of the 3-alkyl derivatives is observed in the remaining solvents. These compounds were isolated with a chromatographic column and identified by alternative synthesis [3].

The alkylation proceeds in two steps. The first step is the formation of rhodanine salts. When rhodanine is alkylated in the presence of triethylamine in ether, hexane, carbon tetrachloride, and benzene, triethylammonium rhodanide is initially formed and precipitates as a crystalline salt which subsequently enters into the alkylation. The rate of alkylation is determined to a considerable degree by the concentration of components in solution, i.e., in the final analysis, by the solubilities of the components. For example, in chloroform with triethylamine as the acceptor all components are soluble, and the reaction with alkyl iodides is complete after 7-9 h at 20-25 deg with yields of 93-95%. In media where the solubilities of the components are low, for example, in hexane and carbon tetrachloride, the reaction proceeds extremely slowly. At 20-25 deg the conversion is 50% after 16-17 days. Heating the reaction mass increases the rate of alkylation, but the major process is accompanied by thermal decomposition of the rhodanine salts, and the yields of alkylation products decrease to 50-30%.

The 2-alkylrhodanines, which have the thiazoline structure [1, 2], were identified by comparison of the R_f values with those of the 2-alkylrhodanines previously [2] synthesized and by hydrolysis in alcoholic hydrochloric acid with the liberation of the corresponding mercaptans and 2,4-thiazolidinediones [4, 5]. In addition, the UV and IR spectra of the 2-alkylrhodanines were compared with those of the corresponding 3-alkyl derivatives and starting rhodanines.

The 3-alkylrhodanines, like unsubstituted rhodanine, have two absorption bands with maxima (252 and 294 nm) which coincide not only with respect to position but also in intensity [6]. The UV spectra of the 2-alkylrhodanines are characterized by only one absorption band with a maximum at 260-267 nm. The UV

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[*] See [9] for communication I.

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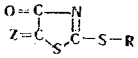
TABLE 1



R	Z	mp, °C	Empirical formula	Found, %				Calculated, %			
				C	H	N	S	C	H	N	S
C_2H_5	H_2	35	$C_5H_7NOS_2$	37,1	4,2	8,4	39,4	37,2	4,3	8,6	39,7
n-C_3H_7	H_2	5	$C_6H_9NOS_2$	41,4	5,3	8,1	36,9	41,1	5,1	7,9	36,5
i-C_3H_7	H_2	2	$C_6H_9NOS_2$	40,9	5,0	8,0	36,7	41,1	5,1	7,9	36,5
n-C_4H_9	H_2	Oil	$C_7H_{11}NOS_2$	48,5	6,0	8,2	36,8	48,8	6,4	8,1	37,2
i-C_4H_9	H_2	Oil	$C_7H_{11}NOS_2$	48,7	6,4	8,0	36,9	48,8	6,4	8,1	37,2
n-C_5H_{11}	H_2	Oil	$C_8H_{13}NOS_2$	47,4	6,5	6,8	31,9	47,2	6,4	6,8	31,5
C_2H_5	C_6H_5CH	110	$C_{12}H_{11}NOS_2$	58,0	4,6	5,6	25,3	57,8	4,4	5,6	25,7
i-C_3H_7	C_6H_5CH	85	$C_{13}H_{13}NOS_2$	59,0	4,8	5,4	24,9	59,2	4,9	5,3	24,3
C_2H_5	p-$O_2NC_6H_4CH$	170	$C_{12}H_{10}N_2O_3S_2$	48,5	3,0	9,7	22,0	48,9	3,4	9,5	21,7
C_2H_5	p-$(CH_3)_2NC_6H_4CH$	198	$C_{14}H_{16}N_2OS_2$	37,4	5,3	9,7	22,2	57,5	5,5	9,5	21,9
CH_3	p-$H_3CC_6H_4CH$	155	$C_{12}H_{11}NOS_2$	57,8	4,4	5,6	25,7	57,8	4,4	5,6	25,7

spectra of the 2-alkyl-5-benzylidenerhodanines at 250-350 nm also differ from the UV spectra of the corresponding 5-benzylidenerhodanines and their 3-alkyl derivatives [1, 7].

The IR spectra of the 2-alkylrhodanines contain an intense band at 1685-1690 cm^{-1}, which we ascribe to the valence vibrations of the carbonyl group conjugated with the C=N bond of the thiazoline ring [8]. The corresponding bands of the unconjugated carbonyl group in the IR spectra of rhodanine, 3-alkylrhodanines, and their 5-benzylidene derivatives are shifted tohigher frequencies (1710-1728 cm^{-1}).

EXPERIMENTAL

2-Methylthio-Δ^2-thiazolin-4-one (2-methylrhodanine). A mixture of 1.33 g (0.01 mole) of rhodanine, 1.01 g (0.01 mole) of triethylamine, and 6.6 g (0.05 mole) of methyl iodide in 30 ml of dioxane was stirred at 20-25 deg for 9 h; half of the solvent was removed by distillation; and the resulting crude 2-methylrhodanine was crystallized from ether–hexane (1:1) to give 1.35 g (92%) of a product with mp 82 deg.

The reaction of rhodanines with various alkyl halides in dioxane was carried out similarly (Table 1).

3-Methylrhodanine. The mother liquor remaining after crystallization of 2-methylrhodanine was placed on a chromatographic column (length 40 cm, diameter 1 cm) filled with activity-I-III (Brockmann) aluminum oxide and eluted with a mixture of hexane and acetone, gradually increasing the percentage of acetone from 0 to 30 vol. %. The solution of 3-methylrhodanine was vacuum-evaporated to three fourths of its initial volume, and the resulting precipitate of 3-methylrhodanine was filtered and dried to constant weight to give 0.07 g (5%) of a product with mp 73-74 deg.

The other 3-alkylrhodanines were similarly isolated.

Thin-layer chromatography was carried out on aluminum oxide modified by boiling in 10% aqueous oxalic acid with subsequent washing until it was neutral, followed by drying at 100 deg for 3 h. The elution system was acetone–hexane–acetic acid (40:120:1).

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